Interactions of ink jet inks with ink jet coatings

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Abstract

Generally, the interactions of ink and coatings in ink jet printing are complex as many parameters are present. The most basic objectives with water based inks is to render printouts waterfast and as lightfast as possible. These are the key functions for color graphics outdoor applications. It is well known that cationic mordants are used to fix anionic dyes in ink jet inks. With the pigmented inks which were introduced very recently the fixation mechanism is different. Furthermore, lightfastness of dye based inks is strongly depending on coating composition.

In this report the main mechanisms of ink-coating interactions will be discussed briefly. Recent results with commercially available inks and selected model coatings are presented with respect to the light stability of dye based as well as pigment based ink jet inks. Influences of UV-light, humidity, Ozone, lamination and coating composition have been investigated.

Introduction

The low stability of ink jet prints has long been the obstacle to outdoor applications. Nevertheless, outdoor applications represent a large market for wide format small edition prints. They can be produced economically by ink jet printing based on water based ink jetted by bubble jet or piezo print heads. With the development and market introduction of improved dye based inks and recently the pigmented ink jet inks a new aera of printing has begun. But, without matched coated print media as well as lamination films the new inks will not be successful.

While waterfastness with dye based inks is realized already by adding cationic mordants in porous coatings which render the anionic dyes insoluble by a cation-anion-complex formation (1), pigments in pigmented inks are easily fixed at the huge inner surface of porous coatings after removal of the dispersing medium water by evaporation. Another approach is to overlaminate water sensitive coatings after printing to protect the print against humidity and water.

It is well known that the fading of dyes and pigments with time in outdoor and indoor daylight is based on different chemical deterioration mechanisms in which UV or visible light as well as oxidation are involved (2). Some Azo-dyestuffs are easily decomposed at the Azo moiety by oxidation after light stimulation. Therefore, oxidation stability of dyes is an important factor for fading of prints (3). In general, pigments are more stable than dyes because of the stability of the cristalline structures which prevent oxidation in the volume of the particles as well as by stabilizing the dye structures in the crystal. Of course, the chemistry of each single dye is a main factor of stability. Magenta dyes and pigments are the most sensitive to irradiation by UV and visible light and therefore the main problem in lightfast printing systems.

The objective of this study was to determine some of these parameters, particularly concerning the interaction between inks, coatings and lamination. Therefore, two different model coatings were chosen which can be regarded as extremes concerning functionality. The first coating is a highly porous coating based on silica, where the ink penetrates very fast into the inner void volume of the coating layer by a viscous flow mechanism. The silica particles are fixed by binders to render the coating itself waterfast. The second coating is based on a water soluble polymer which takes up ink by diffusional processes via swelling. Both coatings were applied to a self adhesive vinyl base.

All materials used were commercially available. This should ensure that the results of this study are as near as possible to practical use.

Experimental

Media:

Two different coatings were applied to a self adhesive white vinyl film with monomeric plasticizer. Coating A is a highly porous, matte coating based on precipitated silica with a BET surface of 300-400 m²/g, cationic mordant (Poly-diallyldimethylammonium-chloride) and organic poly-meric binders. The pH of the coating was adjusted to 7,5. Coating B is a swellable, glossy coating based on polyvinyl alcohol with a saponification degree of 88%. Both coatings are used on commercially available ink jet media from Sihl.

Inks:

Four different water based commercial ink sets (CMYK) were selected to discuss the influences of different dyes and pigments. The dyestuffs were analyzed by visible and UV spectroscopy (4). The following dyes and pigments are used (5):

- Ink set 1 C: Direct Blue 199, M: unidentified, Y: Direct Yellow 132, K: unidentified dye mixture (Encad GA ink)
- Ink set 2 C: Direct Blue199, M: Reactive Red 180, Y: Direct Yellow 132, K: Bayscript N01 from Bayer (Sihl

USA; Spectraprint UV+)

- Ink set 3 C: Pigment Blue 15, M: Pigment Red 23, Pigment Yellow 14, K: carbon black (Sihl USA; Spectraprint pigmented)
- Ink set 4 C: Pigment Blue 15:3, M: Pigment Red 122, Y: Pigment Yellow 128, K: carbon black (Encad; GO-ink)

Printing:

All inks were printed on a Novajet II (Encad) onto both media with solid 100% ink deposition areas of each primary color (CMYK) of appr. 1 inch square with HP cartridges of the type 51625A.

Lamination:

Prints were overlaminated after a minimum drying time of 24 hours with 4 different commercially available cold lamination (self adhesive) films. After lamination the prints were cut at the edges of the colored areas. The lamination films were: Inno-Tack 01-140; Avery Dennison FasCal Fasfitti (if not indicated, this film was used as standard lamination film in this report); MacTac Permagard PG 7036; Korn-Sallmetall Gloss 40. Fig. 1 shows the light absorption characteristics of these lamination films.

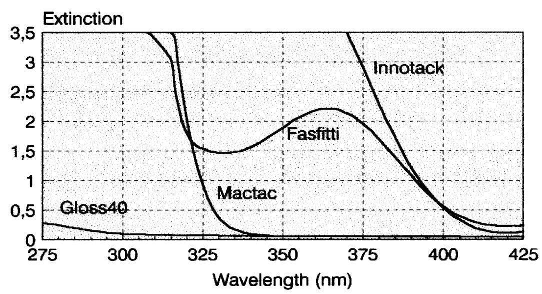

Figure 1. Spectral absorption of lamination films.

Light exposure:

Printed samples were exposed in a Haereus Suntest CPS device with Xenon arc lamp and filter to match standard outdoor daylight (CIE85/1989). The irradiation intensity between 300 nm and 800 nm was 765 W/m², black panel temperature was 45 °C, distance of prints to the axis of the Xenon arc lamp was 230 mm. The printed samples were exposed to the intensive light for up to 144 hours. Before exposure and within short interruption periods during the exposure the optical density of the printed areas was mea-sured with a reflection densitometer MacBeth RD920 with the respective CMYK-filters. The remaining optical density after exposure was calculated as the percentage of density related to the initial density reading (without exposure).

Inks were exposed to light under the same conditions as printed samples. The inks were diluted with pure water to an extinction of 2.6 to 2.8 at the maximum absorption wave-length in the visible light at a path length of 1 cm. The exposure was made in non absorbing, 1 cm thick quarz glass vessels. Relative extinctions (in %) as measure of the residual dye concentration were calculated after different exposure times.

Ozone exposure:

Ozone was generated by purging pure oxygen through a ionization tube O2-GOLD-ION of BIO-KLION Bruno Wertz GmbH/Düren/Germany. Constant flow and optimal ozone yield was achieved by pressurizing with 0.2 bar. All meas-urements were carried out by purging the ozone/ oxygen mixture at 20 °C through the ink via a fine porous glass filter in a 100 ml glass cylinder with a small outlet. 50 ml of the above mentioned diluted inks were filled in. After replacing evaporized water extinctions of the ink solution at the aborption maximum were read after different exposure times with a spectrophotometer. Relative extinctions were calculated with reference to the initial extinction.

Results and Discussion

Ink properties

To characterize the relative stability of the ink solutions without influence of an ink jet receptive coating the diluted ink solutions were investigated under extreme oxidation conditions by an ozone treatment and by exposing to artificial high intensity daylight.

The ozone treatment (Fig. 2) of the inks showed that pigmented ink sets (ink sets 3 and 4) are much more stable to oxidation than dye based inks (ink sets 1 and 2). Single dye molecules in solution are directly exposed to ozone while pigment crystals have to be attacked from the limited particle surface. Differences in the stability are mainly due to the different chemical structures of the dyestuffs, e.g. Magentas of dye inks sets 1 and 2 as well as of pigment ink sets 3 and 4 are very different regarding their stability.

The light induced decomposition of the diluted inks is indicated in Fig. 3. As black dye based inks (K) are complex dyes or compositions of several dyes only the maximum at appr. 560 nm was evalutated. K and C dye ink of ink set 2 are very sensitive to light exposure as well as the M of ink set 1. The other dyes are relatively stable within the inves-tigated exposure period. Pigmented inks (ink sets 3 and 4) have very stable blacks (carbon) and cyans (phthalocyanins) but ink set 3 has extremly sensitive Magenta and Yellow, which are, surprisingly, less stable than dye based inks.

By comparing these results to the light exposure experiments of printed samples (see below) the mechanism of deterioration can be evaluated as well as the influence of coatings. The main difference to the investigation of printed samples is that prints were exposed after drying while in ink exposures the dyes and pigment particles are in close contact with water, which is saturated with oxygen. By UV light initialisation the sensitive dyes and pigments decompose directly by light or after chemical reaction with the surrounding medium (water, oxygen, ink ingredients). At this point a more detailed discussion of these results is not possible. Nevertheless, these results give an indication of the light and oxidation resistance of the investigated inks without interaction of a coating under extremly humid conditions as they can also occur with ink jet prints.

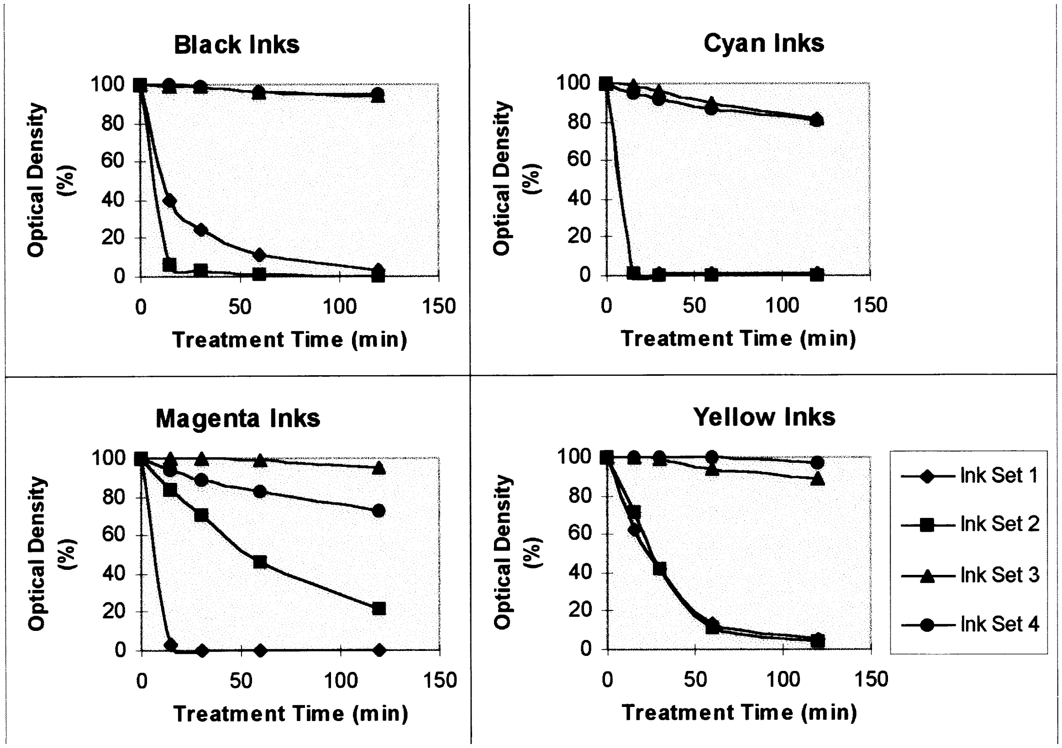

Figure 2: Ozone treatment of diluted inks

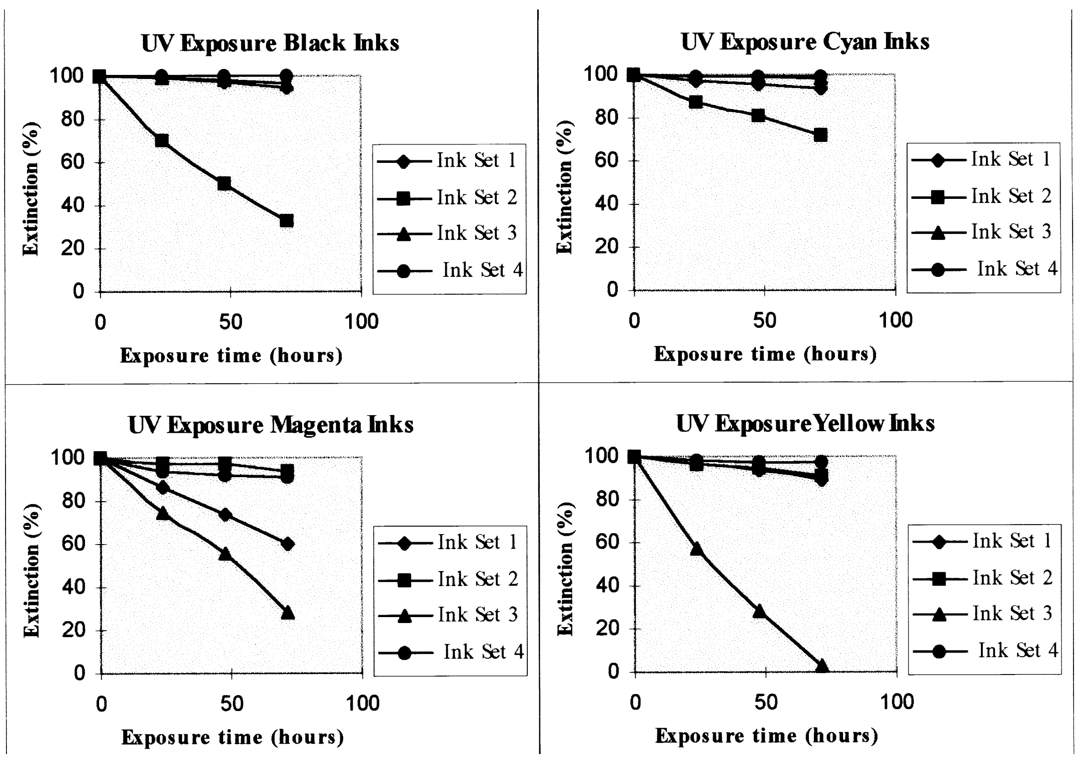

Figure. 3: Light (UV) exposure of diluted inks.

Dye ink set 1 on different media

This ink set is an example for many inks used for indoor graphic arts, office or CAD application (Figs. 4 and 5). The stability under outdoor daylight conditions is very low compared to ink set 4 which is designed for outdoor applications (see below). Magenta is the most critical dye in ink set 1 which cannot be improved neither by selection of a swellable (B) instead of a porous coating (A) nor by overlamination. This means that this dye is extremely sensitive to light induced decomposition (see Fig. 3). As the lamination film effectively absorbs UV light this dye is decomposed directly by visible light of the absoption wavelengths at 560 nm.

C, Y and K are more stable than M. There is a significant improvement in light stability by using the coating B instead of A. This must be due to the nature of the coating. With coating A the dyes are fixed in a ionic complex with the cationic mordant which renders the prints waterfast. The highly porous structure is permeable to air (oxygen) so that the light induced oxidation can take place without restrictions. The lightfastness is worse than that of the inks itselves; this means that the interactions of the dyes with the coating destabilizes the dyes. As the dyes are embedded in the swellable polyvinyl alcohol in coating B - PVA is known to be an excellent barrier for oxygen - both the reduced oxygen concentration as well as the molecular interactions of the PVA coating with the dye molecules may improve light fastness. These results correlate well to the oxidation instability of ink set 1 in the ozone test (Fig. 2).

If UV light is absorbed by overlamination (Fasfitti film) the stability of C, Y and K increases clearly with both coatings A and B. This means that these dyes can be decomposed directly by UV radiation, but to some extent also in case of coating B by initiation with visible light. Nevertheless, the surrounding of the dye molecules is important: coating B results in better stabilities than coating A. As the lamination film does not overlap the print edges gas (air) transport through the porous structure of coating A is not limited as with PVA coating B so that a light induced oxidation can take place.

Dye ink set 2 on different media

With ink set 2 similar fading characteristics depending on coating and overlamination are found (Figs. 6 and 7) as with ink set 1 with the exception of the Magenta ink. This M dye is much more stable to visible light than that of ink set 1 because UV absorbing overlamination is able to improve the lightfastness of the prints particularly on coating B. Prints of C, Y and K on coating B with overlamination are more lightfast because of the effective UV absorption by the lamination film and because of the stabilization by the coating in which dyes are embedded and protected from reaction with oxygen. This is supported by the ozone treatment results (Fig. 2) and the ink UV exposure results (Fig. 3) in which Magenta of ink set 2 is more stable than Magenta of ink set 1.

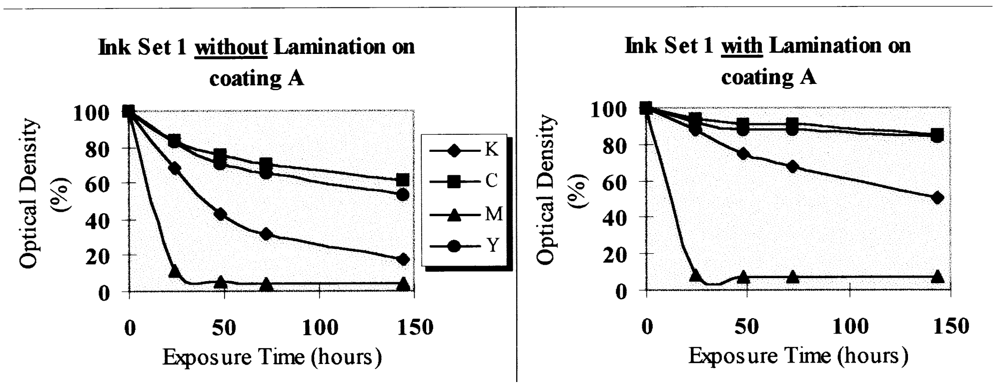

Fig. 4: Accelerated light exposure of ink jet prints with ink set 1 on coating A.

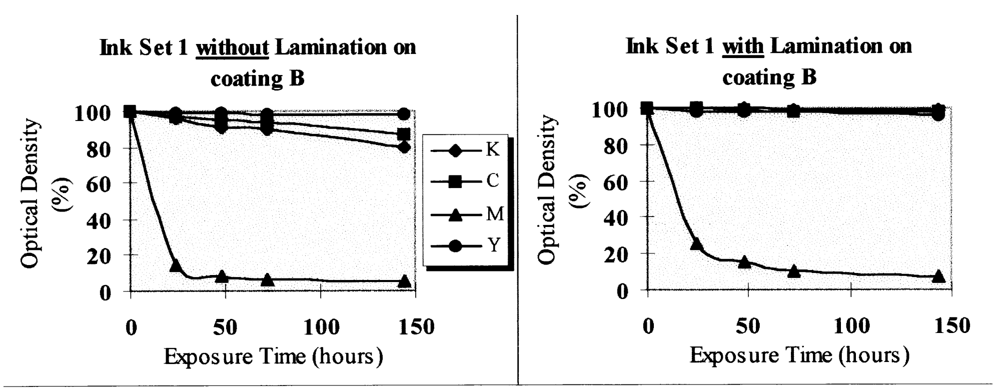

Fig. 5: Accelerated light exposure of ink jet prints with ink set 1 on coating B.

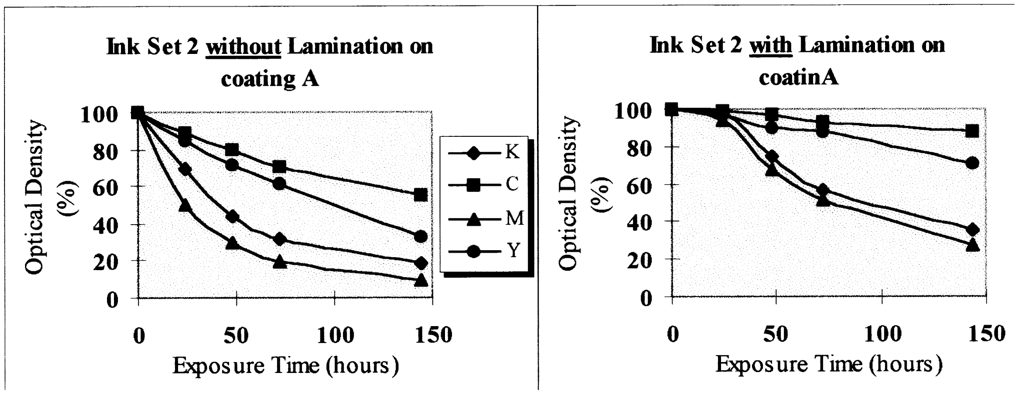

Fig. 6: Accelerated light exposure of ink jet prints with ink set 2 on coating A.

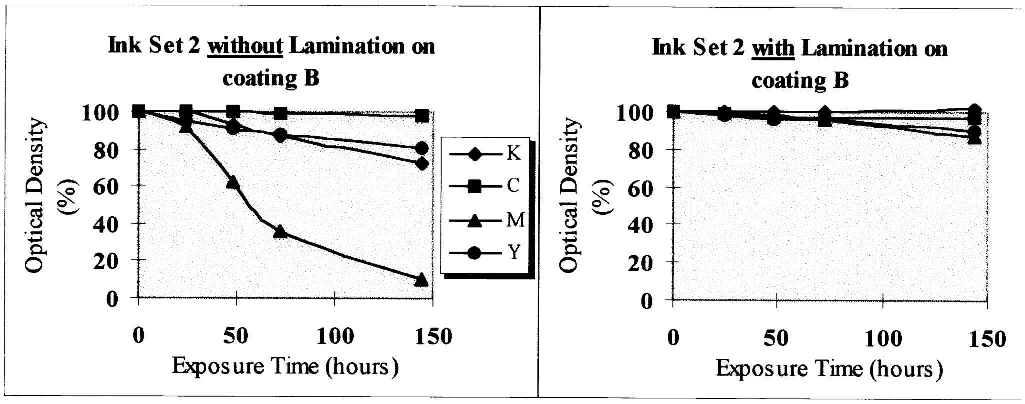

Fig. 7: Accelerated light exposure of ink jet prints with ink set 2 on coating B.

With lamination, ink set 2 is very lightfast on coating B. Even the less light stable K and C inks (Fig.3) are rendered highly lightfast by this coating after overlamination, presumably because of stabilizing the dyes against oxidation.

Influence of different lamination films

The influence of different lamination films was studied after light exposure of prints with ink set 2 for 144 hours on coating A (Tab. 1).

Table 1 Optical densities in % of initial density of CMYK prints on *coating A* with ink 2 using different lamination films

Lamination Film	C	M	Y	K
Inno-Tack 0140	97	33	81	51
Avery FasFitti	98	27	79	50
MacTac 7036	89	24	76	47
Sallmetall Gloss 40	73	8	64	30
without lamination	55	9	32	18

It is evident that lamination is more effective when more UV light is absorbed by the lamination film (from top to bottom the UV absoption of the lamination films decreases, s. Fig. 1). All colors (CMYK) are affected in the same way but to different degrees. UV light in the wavelength range of 280 nm to 320 nm is the most critical. This wavelength range is not absorbed by the Mactac film. Nevertheless, none of the studied dye based inks can be used for outdoor applications with coating A because fading of M, Y and K is too fast even after overlamination.

The same investigation was made with coating B. Again, high UV absorption of the lamination film improves lightfastness. With FasFitti lamination film optimal results are given, even with Magenta which is much more stable in combination with the coating B. These results clearly show that some dyes need optimum conditions concerning coating formulation and lamination to render prints as lightfast as possible.

Table 2 Optical densities in % of initial density of CMYKprints on *coating B* with ink 2 using different lamination films

Lamination Film	C	M	Y	K
Avery FasFitti	96	88	90	100
MacTac 7036	98	40	94	87
Sallmetall Gloss 40	96	11	79	85
without lamination	98	10	80	76

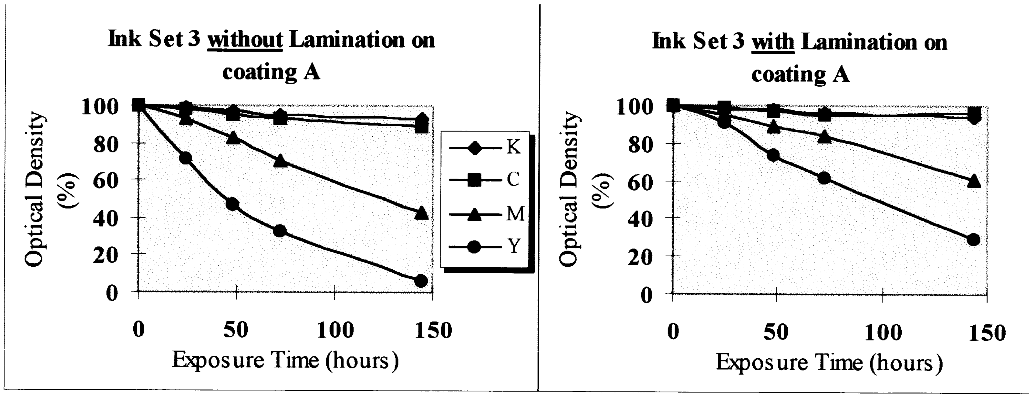

Fig. 8: Accelerated light exposure of ink jet prints with ink set 3 on coating A.

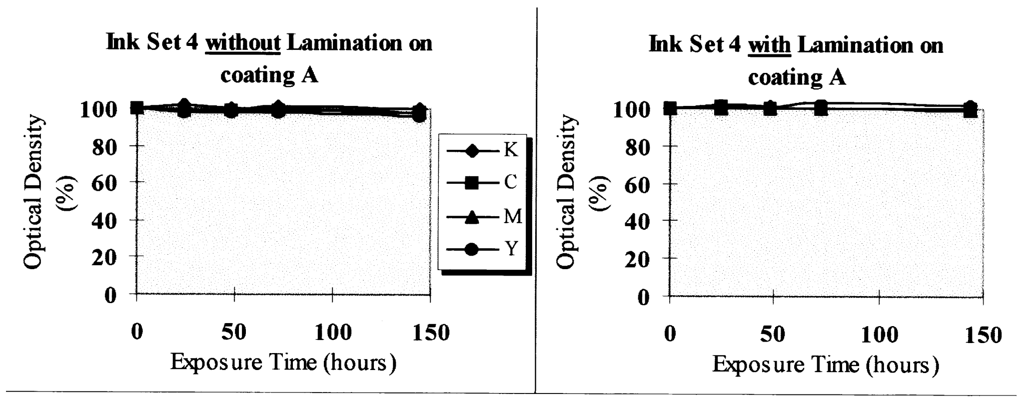

Fig. 9: Accelerated light exposure of ink jet prints with ink set 4 on coating A.

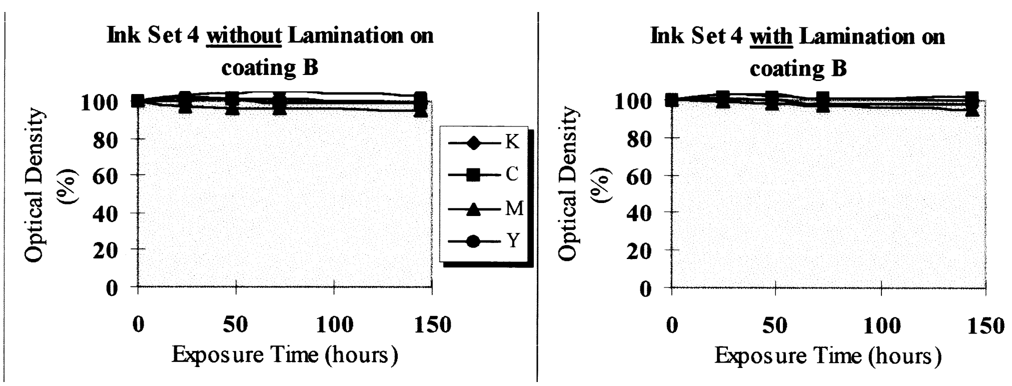

Fig. 10: Accelerated light exposure of ink jet prints with ink set 4 on coating B.

Lightfastness of pigmented inks on different media

Both pigmented ink sets 3 and 4 are printed on the porous, matte ink accepting layer (coating A). During printing the pigments penetrate into the porous structure of the coating and become waterfast after evaporation of the carrier liquid (water) and fixation on the inner surface of the coating. The lightfastness of the printed inks (Figs. 8 and 9) is evaluated with and without lamination. Ink set 3 is unstable in M and Y as was found in the light exposure experiments on the diluted inks of ink set 3 (Fig. 3). As the exposure took place under very dry conditions these pigments seem to be directly decomposed by absorption of light. Humidity or water does not seem to play an important role for deterioration of these pigments.

Lamination of printed areas of ink set 3 improves the light fastness by about a factor of 2 for Y (same optical density loss after double of exposure time) but not as strong on M. As UV light is effectively shielded by the lamination film (Fasfitti) Y seems to be more UV sensitive than M which may be mainly destroyed by visible light. Therefore, in case of ink set 3 lamination is not really helpful to improve light stability for outdoor application.

Ink set 4 is the most stable in this investigation (Figs. 9 and 10).

Coating B does not take up the pigments in the coating as swellable coatings allow only small molecules like water to penetrate but none of the pigment particles with diameters in the range of appr. 100 nm. Therefore, the pigment particles lay on the surface and can be easily smeared.

Within the chosen exposure period there is no change in optical density of the printed areas. The stability of these pigments is excellent and independent from coating formulation or on lamination. These inks seem to be usable for outdoor applications even without lamination in case of a waterfast coating as realized with coating A.

Conclusions

The main results of this study show that particularly for dye based inks a precise match of all printing components is neccessary to impove lightfastness of prints to a high level. This means that optimum conditions are given by

- selecting proper ink dyes with high oxidation and light (UV and visible) stability,
- printing on a non-porous coating which is able to embed dyes into the polymer and to stabilize dyes by the right chemistry and by protection from oxygen from air,
- overlamination with UV absorbing films.

It was found that porous structures and coating-dye-interactions are able to impact the light sensitivity of some dyes very strongly.

With pigmented ink the selection of pigments is the most critical factor for light stability.

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